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THE LOSS OF CO_2 IN EPOXYCHRYSANTHENONE UNDER ELECTRON IMPACT

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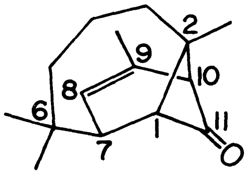
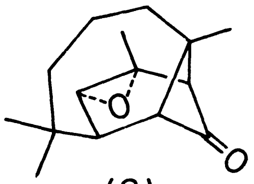
Mass spectra of four kinds of bicyclic β,γ-epoxyketones containing *gem*-dimethyl group were examined. Epoxyvulgarone A and epoxychrysanthenone showed characteristic $[M-C_2H_3O]^+$ and $[M-CO_2]^{+\cdot}$ ions, while the remaining epoxyketones were abundant only in the $[M-C_2H_3O]^+$ ion. The ion kinetic energy-defocusing technique revealed that the loss of CO_2 from the molecular ion occurs *via* a lactone type intermediate.

We have recently isolated a novel sesquiterpene ketone, vulgarone A, from *Chrysanthemum vulgare* (L.) Bernhardi and determined the structure to be 2,6,6,9-tetramethyltricyclo[5.4.1.$0^{2,10}$]undec-8-en-11-one (1).[1a,b] In connection with the structural determination, epoxyderivatives of this ketone and three related ketones were prepared by treating with *m*-chloroperbenzoic acid to examine the mass spectra. Although mass fragmentations of α,β-epoxyketones have been reviewed by Budzikiewicz *et al.*,[2] those of β,γ-epoxyketones have not been reported up to date.



(1)



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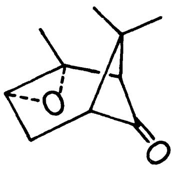

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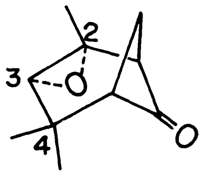

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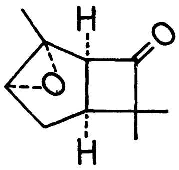

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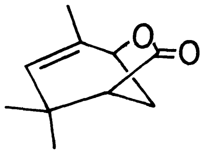


(6)

The mass spectra of the epoxyketones are reproduced in Fig.[3] Among them, epoxyvulgarone A (2) and epoxychrysanthenone (3) showed in common two characteristic peaks of [M-43] and [M-44] ions with considerable intensities at m/e 191 (10%) and 190 (26%) and at m/e 123 (15%) and 122 (18%), although they were somewhat different in the relative intensities between both compounds. On the other hand, in the mass spectra of 2,4,4-trimethylbicyclo[3.1.1]heptan-2,3-epoxy-6-one (4),[4] which is an

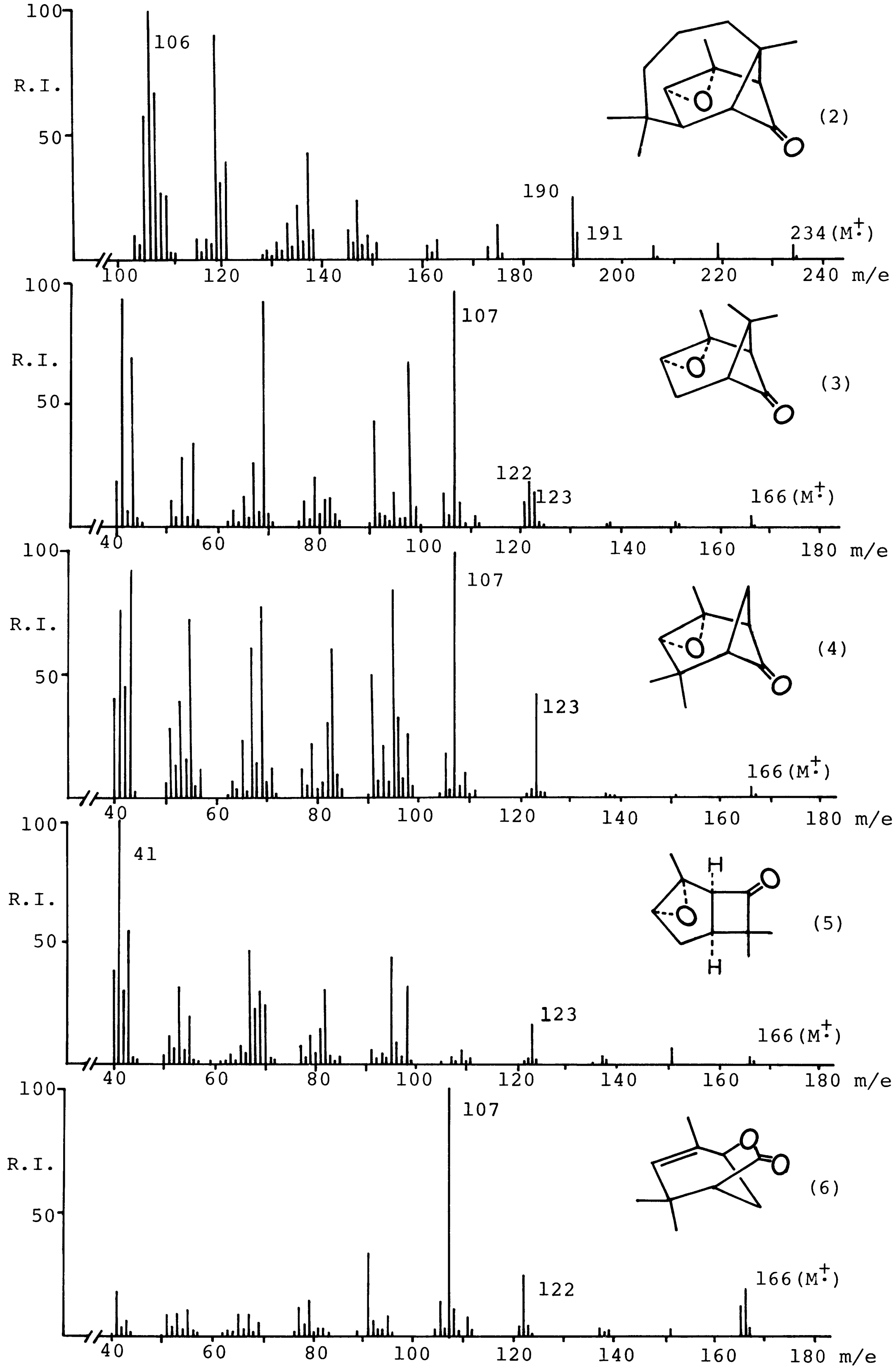
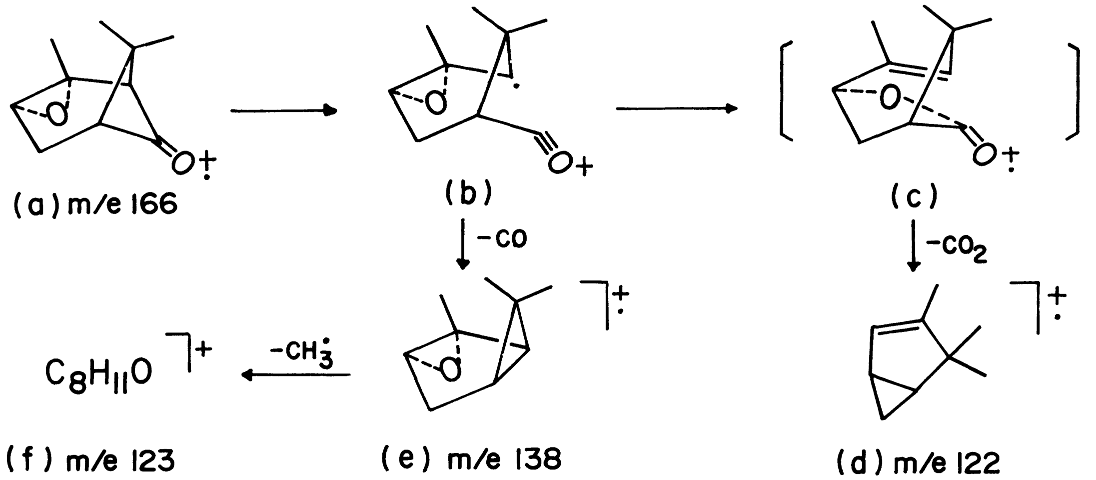

100
R.I.
50
106
190
191
234($M^{+\cdot}$)
(2)
100
120
140
160
180
200
220
240 m/e
100
R.I.
50
107
122
123
166($M^{+\cdot}$)
(3)
40
60
80
100
120
140
160
180 m/e
100
R.I.
50
107
123
166($M^{+\cdot}$)
(4)
40
60
80
100
120
140
160
180 m/e
100
R.I.
50
41
123
166($M^{+\cdot}$)
H
H
(5)
40
60
80
100
120
140
160
180 m/e
100
R.I.
50
107
122
166($M^{+\cdot}$)
(6)
40
60
80
100
120
140
160
180 m/e

Fig.

isomer of epoxychrysanthenone differing only in the position of the *gem*-dimethyl group, and epoxyfilifolone (5),[5] which has a carbon skeleton differing completely in the fused system, the [M-43] ions were comparatively abundant and the [M-44] ions were very weak. The elemental compositions of the ions were determined by high resolution mass measurements[3] and they were characterized as $[M-C_2H_3O]^+$ and $[M-CO_2]^{+\cdot}$ ions. Furthermore, the metastable ions corresponding to the transition from the molecular ion to the $[M-CO_2]^{+\cdot}$ ion were respectively detected in compounds 2 and 3 as dish-topped metastable peaks centered at m* 154.5 (electric sector voltage ratio (γ) of 0.8125, calcd. m* 154.4; γ=0.8121) and m* 89.7 (γ=0.7350, calcd. m* 89.8; γ= 0.7352) by the ion kinetic energy-defocusing technique.[3,6,7] We were interested in the fact that CO_2 was directly lost from the molecular ion of such β,γ-epoxyketones as carbonyl and epoxy groups are located far a part.

It has been reported[8] that in the photochemical reaction the skeletal framework of 7-oxabicyclo[4.1.0]heptan-3-one, that is, a cyclic β,γ-epoxyketone, isomerized easily to an unsaturated γ-lactone. Furthermore, a photochemical reaction of epoxychrysanthenone gave filifolide A (6) in a high yield (82%), which showed an abundant peak due to the $[M-CO_2]^{+\cdot}$ ion at m/e 122 and a very weak peak of the $[M-C_2H_3O]^+$ ion at m/e 123 as shown in Fig. in contrast to those of the other β,γ-epoxyketones (4 and 5). Difference of spectral patterns between compounds 3 and 6 indicated that the former did not isomerize to the latter by electron impact, whereas the metastable ion corresponding to the transition from the molecular ion to the $[M-CO_2]^{+\cdot}$ ion was detected as a gaussian peak centered at m* 89.9 (γ=0.7355, calcd. m* 89.8; γ=0.7352) in the compound 6. From these results, the loss of CO_2 in the β,γ-epoxyketones (2 and 3) is considered to occur *via* a lactone type intermediate. Accordingly, the fragmentation pathway of the $[M-CO_2]^{+\cdot}$ ion on the compound 3 under electron impact may be rationalized using a γ-lactone type intermediate as follow. The initial α-cleavage of carbonyl group in the molecular ion gives ion (b). The ion thus produced, after being converted to ion (c) of a γ-lactone intermediate, releases CO_2, yielding the ion (d), as the structures have already been reported[9] in a photochemical reaction of chrysanthenone. On the other hand, formation of the $[M-C_2H_3O]^+$ ion (f) was thought to be produced by loss of CO followed by loss of a methyl radical from the ion (b) and/or by loss of a methyl radical and subsequent CO.



The intensities of $[M-CO_2]^{+\cdot}$ ions observed in the β,γ-epoxyketones may be attributable to the facility of formation of the lactone type intermediate. The structures of the compounds, 4 and 5, prevent respectively the formation by the neighboring *gem*-dimethyl group adjacent to epoxy oxygen and by *trans*-configuration of the epoxy oxygen and carbonyl group.

This is an interesting example showing the close connection between the mass fragmentation and the photochemical reaction.

References and Notes

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3) The high resolution mass spectra were taken using an on-line system which combined a HITAC-10 computer with a Hitachi RMU-7L double focusing mass spectrometer: ionizing energy 70 eV, ionizing current 80 μA, and accelerating voltage 3.2 kV. Relative intensities of fragment ions calculated based on ordinary mass spectra taken by a Hitachi RMS-4 mass spectrometer: ionizing energy 70 eV, ionizing current 80 μA, and accelerating voltage 1.5 kV. The metastable ions were examined on the RMU-7L modified with a metastable defocusing attachment.

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